Dearomatized BIAN Alkaline Earth Alkyl Catalysts for the Intramolecular Hydroamination of Hindered Aminoalkenes

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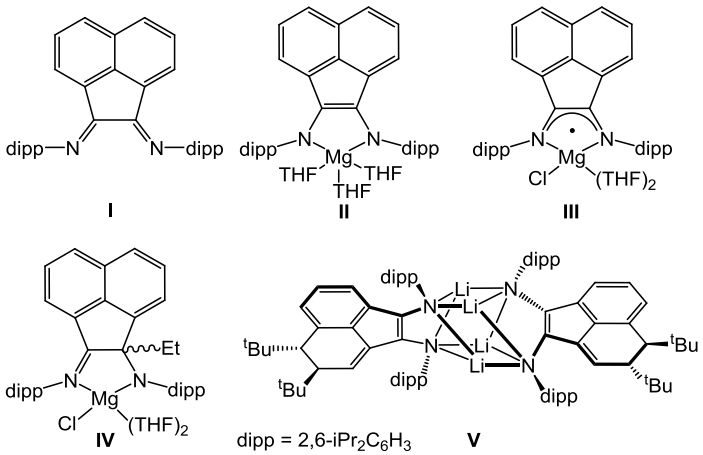
Abstract

Reaction of a sterically encumbered bis(imino)acenapthene (dipp-BIAN) with either potassium alkyl or heavier alkaline earth dialkyl, [Ae{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (Ae = Mg, Ca, Sr), reagents results in deromatization of the aromatic ligand. The heteroleptic alkaline earth alkyl species show enhanced stability toward Schlenk-type redistribution but undergo solution exchange when the bis(trimethylsilyl)methyl substituent is replaced by an anionic ligand of lower overall steric demands. In contrast analogous reactions performed with [Ba{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] evidenced facile solution redistribution and resulted in an unusual C-C coupling reaction which is suggested to result from a sterically induced reductive process. An assessment of the Mg, Ca, and Sr alkyl compounds as precatalysts for the intramolecular hydroamination of aminoalkenes evidenced enhanced reactivity which is ascribed to the greater solution stability of the catalytically active species. Most notably the calcium species may even be applied to the high yielding cyclization of substrates bearing alkyl substitution at either of the alkenyl positions.

Introduction

In the catalogue of readily available coordinating α-diimines, bis(imino)acenaphthene (BIAN) ligands such as **I** have gained some prominence over the last two decades. Although first reported in the 1960s,[1] the use of this class of ligand only became popular in the late 1990s.



I II III IV V

The ability of neutral BIAN ligands to act as strong and rigid chelators for metals in a variety of oxidation states has given rise to a rich transition metal coordination and catalytic chemistry.[2] In particular, Elsevier and co-workers have reported the use of palladium and platinum aryl-BIAN complexes for catalytic C–C bond formation, hydrogenation and hydrosilylation reactions,[3] while Brookhart[4] and Coates[5] have demonstrated the efficiency of cationic nickel(II), palladium(II) and platinum(II) aryl-BIAN precatalysts in the polymerization of olefins. Due to the presence of the naphthalene backbone, BIAN ligands may also act as electron acceptors in the presence of strongly reducing metals. For example the addition of one, two, three or four equivalents of elemental sodium to **I** respectively yields the mono-, di-, tri- and tetra-anionic salts $[\{\mathbf{I}\}^{n-}\{Na_n(S)_m\}^{n+}]$ (n = 1–4, S = Et_2O, THF).[6] This chemistry, extended to s- and p-block metals,[7] and, more recently, to f-block elements,[8] has been extensively explored by the group of Fedushkin.

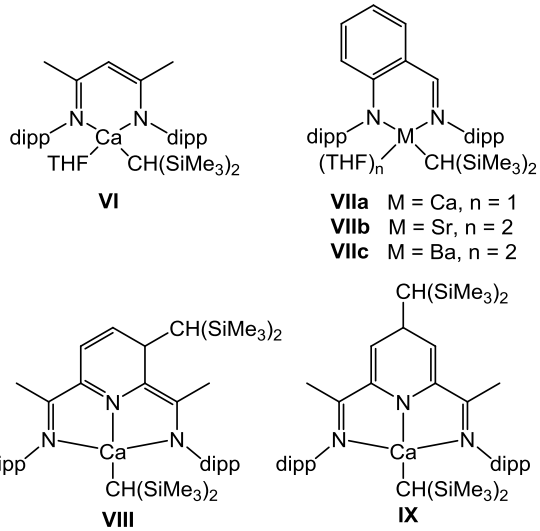
The redox properties of the BIAN ligand have also led to some unusual reactivity for main group and, of most relevance to the current work, group 2 complexes. The magnesium species $[\{\mathbf{I}\}Mg(THF)_3]$, **II**, for example, has been shown to act as a reducing agent for non-enolizable ketones *via* single electron transfer to form the corresponding magnesium alkoxide radical-anion complex.[9] Oxidation of complex **II** by halogenated tin, copper, mercury or silicon reagents led to the isolation of radical-anion magnesium halides, such as compound **III**.[10] Furthermore, compound **II** and its strontium and barium analogues have also been shown to deprotonate acidic substrates such as enolizable ketones,[11] phenylacetylene[12] or *α*-

acidic nitriles[13] to give the corresponding enolate, acetylide or keteniminate group 2 complexes of the protonated monoanionic amine-amido ligand **I-H**$^-$. Alkylation of the BIAN imine carbon has also been observed in the reaction between **II** and ethyl halides, which resulted in the formation of complex **IV** via ethylation of the carbon adjacent to the amide functionality.[14] The mechanism proposed by the authors for the formation of this compound involves a single electron transfer from **II** to the ethyl halide, yielding the intermediate radical-anion magnesium halide complex, **III**, and Et$^\bullet$, followed by radical attack of Et$^\bullet$ to form complex **IV**. A similar alkyl transfer has also been observed in the reaction between ^{n}BuLi or MR_3 (M = group 13 metal, R = alkyl substituent) and **I** in non-coordinating solvents, leading to the formation of a imine-amido complex bearing an alkyl substituent on the carbon adjacent to the amide functionality.[15] More recently Cowley and co-workers also reported the double alkylation of the acenaphthene backbone of **I** in the C^4 and C^5 positions by *tert*-butyllithium, via a radical dearomatization, two-electron reduction pathway, leading to the formation of complex **V**.[16]

Our studies have focused on the coordination chemistry and catalytic properties of hitherto understudied alkaline earth complexes.[17] While rapid progress has been made over the past decade one major challenge remains the stabilization of heteroleptic species of the type [LAeR] (L = monoanionic ligand, Ae = alkaline earth dication, R = reactive co-ligand) as the heavier alkaline earth metal complexes are prone to Schlenk-type ligand redistribution processes in solution, which hamper catalytic activity.[18] Examples of heteroleptic group 2 alkyl complexes remain particularly rare as many conventional ligand systems, such as the ubiquitous *β*-diketiminate ligand $[HC\{C(Me)Ndipp\}_2]^-$ (dipp = 2,6-di-*iso*-propylphenyl), are prone to deprotonation reactions by the highly reactive alkaline earth-bound alkyl functionality.[19] Thus only the calcium *β*-diketiminato bis(trimethylsilyl)methyl derivative, **VI**, could be prepared from the reaction between $[\{HC\{C(Me)Ndipp\}_2\}H]$ and the homoleptic precursor $[Ca\{CH(SiMe_3)_2)_2(THF)_2]$.[19b] Harder and co-workers have also reported several heteroleptic calcium, strontium and barium benzyl complexes for the catalytic polymerization of styrene.[20] More recently Carpentier and Sarazin have described a series of analogous heteroleptic heavier alkaline earth alkyl complexes, compounds **VIIa-c**, supported by a sterically demanding iminoanilide ligand, and reported their successful application as precatalysts for intra- and intermolecular hydroamination reactions.[21]

We have reported that bis(imino)pyridine ligands undergo double deprotonation of the *β*-imino-methyl substituents in the presence of the alkaline earth dialkyls $[M\{CH(SiMe_3)_2\}_2(THF)_2]$ (M = Mg, Ca, Sr, Ba). In the case of the calcium, strontium and

barium precursors this reaction proceeded via the formation of intermediate, unstable, heteroleptic alkaline earth alkyl complexes, such as **VIII** and **IX**, supported by a *meta*- or *para*-alkylated dearomatized (imine-amido)dihydropyridine ligand.[22] A similar strategy had already been employed to obtain heteroleptic dihydroterpyridide lanthanide alkyl complexes in a selective alkylation/dearomatization reaction.[23]



We have previously described in preliminary form, dearomatization reactions of dipp-substituted bis(imino)acenaphthenes with group 1 and group 2 derivatives of the sterically demanding bis(trimethylsilyl)methyl anion.[24] In this contribution we provide a complete description of this reactivity and the application of the resultant heteroleptic group 2 species for the intramolecular hydroamination of hindered aminoalkenes.

Experimental

General procedures. All glassware was dried for 24 hours in an oven at 150 °C prior to use.Solvents for air- and moisture-sensitive reactions were provided by an Innovative Technology Solvent Purification System. Hexane and toluene were used as collected. THF and diethyl ether were dried by distillation over sodium-benzophenone ketyl. All solvents were stored under argon over molecular sieves activated at 150 ^{o}C *in vacuo*. C_6D_6 and d_8-toluene were purchased from Fluorochem and dried over molten potassium prior to vacuum transfer into a sealed ampoule and storage in the glovebox under argon. (Tetrakis(trimethylsilyl))silane (TMSS) was purchased from Goss Scientific Instruments Ltd. and used as received. After drying over CaH_2 all aminoalkenes were distilled *in vacuo* and either vacuum transferred into sealed ampoules or freeze-dried prior to transfer into the glovebox. The aminoalkene substrates,[25] the ligand precursor, **I**,[2g] the potassium precursors [KCH_2Ph][26] and [$KCH(SiMe_3)_2$],[27] and the homoleptic group 2 alkyls,

$[M\{CH(SiMe_3)_2\}_2(THF)_2]$, (M = Mg, Ca, Sr, Ba)[28] were synthesized following literature procedures. Reactions were carried out under argon atmosphere using standard Schlenk line and glovebox techniques in an MBraun Labmaster glovebox at O_2, H_2O < 0.1 ppm. NMR experiments were conducted in Youngs tap NMR tubes prepared and sealed in a glovebox under argon. NMR data was acquired at room temperature on a Bruker 300 Ultrashield™ (^{13}C, 75.48 MHz) and spectra were referenced using residual solvent resonances. Elemental analyses were performed by Stephen Boyer at London Metropolitan Enterprises.

Synthesis of compounds 1–9 (The numbering scheme used for the NMR assignments of compounds **1**–**9** follows that in Scheme 2.)

*Synthesis of **1***. 25 mg of $[KCH(SiMe_3)_2]$ (99.8 μmol) and 50 mg of **I** (99.8 μmol) were dissolved in C_6D_6. The reaction mixture instantly turned dark green (NMR yield > 99%). Green crystals suitable for X-ray crystallography were isolated upon crystallization from toluene at room temperature. The reaction was later scaled up in toluene with $[KCH(SiMe_3)_2]$ (396 mg, 2.00 mmol) and **I** (1.00 g, 2.00 mmol), 95% isolated yield (1.32 g, 1.90 mmol). ^1H NMR ppm (C_6D_6): 7.00–7.21 (m, 6H, Ar-*H*), 6.51 (d, 1H, *H-3′*, ^3J = 7.5 Hz), 6.03 (t, 1H, *H-4′*, ^3J = 7.5 Hz), 5.65 (d, 1H, *H-5′*, ^3J = 7.5 Hz), 5.60 (d, 1H, *H-3*, $^3J_{cis}$ = 9.8 Hz), 4.65 (dd, 1H, *H-4*, $^3J_{cis}$ = 9.8 Hz, ^3J = 4.1 Hz) , 4.41 (broad, 1H, *H-5*), 3.59-3.60 (m, 2H, ^{i}Pr-C*H*Me$_2$), 3.06 + 2.98 (two sept, 1H each, ^{i}Pr-C*H*Me$_2$, ^3J = 6.7 Hz), 1.51 + 1.44 (two d, 3H each, ^{i}Pr-C*H*$_3$, ^3J = 6.7 Hz), 1.23 + 1.17 + 1.13 (three d, 9H: 3H: 6H, ^{i}Pr-C*H*$_3$, ^3J = 6.7 Hz), 0.55 (s, 1H, CC*H*(SiMe$_3$)$_2$), 0.18 + 0.04 (two s, 9H each, CCH(Si*Me*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ppm (C_6D_6): 175.7 (*C-1′*), 153.9, 152.5, 148.7, 148.5, 141.8, 141.6, 136.6, 136.4, 129.9, 128.2, 127.9, 125.4, 124.4, 124.2, 123.7 (*C-5′* + *C-3*), 123.1, 123.0, 122.9, 121.2 (*C-4′*), 120.4, 116.8 (*C-4*), 102.7, 38.5 (*C-5*), 29.1 + 28.9 + 28.6 + 28.5 (^{i}Pr-*C*HMe$_2$), 25.2 (C*C*H(SiMe$_3$)$_2$), 24.9 + 24.7 + 24.6 + 24.4 + 23.9 + 23.8 (^{i}Pr-*C*H$_3$), 2.3 + 2.1 (CCH(Si*Me*$_3$)$_2$). Anal. Calc. for $C_{43}H_{59}KN_2Si_2$ (699.2): C, 73.86; H, 8.51; N, 4.01%. Found: C, 73.79; H, 8.59; N, 3.96%. ESI-MS for the protonated dearomatized ligand $[C_{43}H_{60}N_2Si_2–Na]^+$: calc. 683.41928; exp. 683.4846.

*Synthesis of **2***. [K{CH(SiMe$_3$)(2-NMe$_2$-Ph)}] (25 mg, 83.5 μmol) and **I** (42 mg, 83.5 μmol) were dissolved in d_8-toluene. The solution instantly turned dark green. Crystallization after one day at room temperature afforded dark green crystals of the (*R*,*S*) + (*S*,*R*) diastereomer of complex **2** (51 mg, 68.3 μmol 82%). ^1H NMR ppm (d_8-tol) of the major (*R*,*S*) + (*S*,*R*) diastereomer (88%): 6.88–7.20 (m, 10H, Ar-*H*), 6.04 (d, 1H, *H-3′*, ^3J = 7.7 Hz), 5.60 (t, 1H,

H-4', ^{3}J = 7.7 Hz), 5.44–5.50 (m, 2H, *H-3/5'*), 4.63–4.67 (m, 1H, *H-4*), 3.81 (broad s, 1H, *H-5*), 3.49 (sept, 2H, ^{i}Pr-C*H*Me$_2$, ^{3}J = 6.7 Hz), 3.35 (s, 1H, C*H*(SiMe$_3$)), 2.95 (sept, 1H, ^{i}Pr-C*H*Me$_2$, ^{3}J = 6.6 Hz), 2.85 (broad m, 1H, ^{i}Pr-C*H*Me$_2$), 2.33 (s, 6H, N*Me$_2$*), 1.52 (d, 3H, ^{i}Pr-C*H$_3$*, ^{3}J = 6.6 Hz), 1.30–1.44 (m, 6H, ^{i}Pr-C*H$_3$*), 0.98–0.19 (m, 12H, ^{i}Pr-C*H$_3$*), 0.81 (d, 3H, ^{i}Pr-C*H$_3$*, ^{3}J = 6.7 Hz), –0.03 (s, 9H, Si*Me$_3$*); minor (*R,R*) + (*S,S*) diastereomer (12%): 6.66 (d, 1H, *H-3'*, ^{3}J = 7.7 Hz), 5.85–5.88 (m, 1H, *H-4'*), 3.46–3.49 (m, 1H, *H-3/5'*), 4.78 (broad d, 1H, *H-4*, $^{3}J_{cis}$ = 10.1 Hz), 3.81 (broad s, 1H, *H-5*), 3.53 (m, 2H, ^{i}Pr-C*H*Me$_2$ + C*H*(SiMe$_3$), identified by COSY), 2.95 + 2.85 (two broad sept, 1H each, ^{i}Pr-C*H*Me$_2$), 2.45 (s, 6H, N*Me$_2$*), 0.99–1.57 (m, 24H, ^{i}Pr-C*H$_3$*), 0.00 (s, 9H, Si*Me$_3$*). ^{13}C{^{1}H} NMR ppm (d$_8$-tol), mixture of both diastereomers: 174.1 (*C-1*), 153.2, 152.6, 148.0, 141.1, 140.8, 140.1, 137.8, 137.7, 137.6, 137.2, 137.1, 136.1, 135.1, 132.1 (*C-3'*), 128.1, 125.3, 123.8, 123.7, 123.5, 123.0 (*C-3/5'*), 122.5 (*C3/5'*), 120.7, 119.3 (*C-4'*), 111.8 (*C-4*), 45.1 (N*Me$_2$*), 42.1 (C-5), 40.1 (*C*H(SiMe$_3$)), 29.2 +29.1 + 28.8 + 28.4 (^{i}Pr-*C*HMe$_2$), 25.7 + 25.2 + 25.1 + 24.5 + 24.4 + 24.2 + 23.5 + 23.4 + 23.2 (^{i}Pr-*C*H$_3$), –0.04 (Si*Me$_3$*). Anal. Calc. for $C_{288}H_{360}K_6N_{18}Si_6$ (4477.14): %C, 77.26; H, 8.10; N, 5.63. Found: %C, 77.22; H, 8.19; N, 5.58.

*Synthesis of **3***. 50 mg of [Mg{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (103.9 μmol) and 52 mg of **I** (103.9 μmol) in C$_6$D$_6$. The reaction mixture was heated at 60 ^{o}C overnight and slowly turned dark green. Analysis by ^{1}H NMR spectroscopy showed the clean formation of complex **3** as the sole product of the reaction (NMR yield > 99%). The reaction was scaled up ([Mg{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] 271 mg, 0.599 mmol; **I** 300 mg, 0.599 mmol) and heated for 24 hours at 60 ^{o}C in toluene prior to removal of the solvent *in vacuo*. As the product refused to crystallize in 0.2 mL of pentane at –30 ^{o}C over a period of several weeks, complex **3** was used as a crude green solid, whose purity was confirmed by NMR and elemental analysis data. ^{1}H NMR ppm (C$_6$D$_6$): 7.15–7.25 (m, 6H, Ar-*H*), 6.45 (d, 1H, *H-3'*, ^{3}J = 7.7 Hz), 6.05 (t, 1H, *H-4'*, ^{3}J = 7.7 Hz), 5.47 (dd, 1H, *H-3*, $^{3}J_{cis}$ = 10.2 Hz, ^{4}J = 2.3 Hz), 5.44–5.47 (m, 1H, *H-5'*), 5.05 (dd, 1H, *H-4*, $^{3}J_{cis}$ = 10.2, ^{3}J = 4.4Hz), 4.07 (m, 1H, *H-5*), 3.78 (broad m, THF), 3.55 + 3.11 (two sept, 2H each, ^{i}Pr-C*H*Me$_2$, ^{3}J = 6.8 Hz), 1.41–1.44 (m, 14H, ^{i}Pr-C*H$_3$* + THF), 1.39 + 1.36 + 1.31 + 1.29 + 1.16 + 1.13 (six d, 3H each, ^{i}Pr-C*H$_3$*, ^{3}J = 6.8 Hz)), 0.46 (d, 1H, CC*H*(SiMe$_3$)$_2$, ^{3}J = 1.6 Hz), 0.00 (s, 18H, MgCH(Si*Me$_3$*)$_2$), 0.01 + –0.03 (two s, 9H each, CCH(Si*Me$_3$*)$_2$), –1.59 (s, 1H, MgC*H*(SiMe$_3$)$_2$). ^{13}C{^{1}H} NMR ppm (C$_6$D$_6$): 181.9 (*C-1'*), 149.5, 148.8, 148.2, 146.5, 144.5, 139.5, 139.4, 133.1, 133.0 (*C-3'*), 131.8, 127.2, 126.0, 125.8 (*C-4*), 125.2, 124.9, 124.8 (*C-5'*), 124.6, 124.5, 124.0, 123.4 (*C-4'*), 122.6 (*C-3*), 122.1, 111.8 (*C-2*), 68.9 (THF, very broad), 38.4 (*C-5*), 29.1 + 28.9 + 28.6 + 28.6 (^{i}Pr-*C*HMe$_2$), 25.9

+ 25.33 + 25.29 + 25.27 + 25.1 + 24.9 + 24.8 + 24.7 (^{i}Pr-*C*H$_3$), 23.9 (THF), 22.7 (C*C*H(SiMe$_3$)$_2$), 5.6 (MgCH(Si*Me*$_3$)$_2$), 2.1 + 1.0 (CCH(Si*Me*$_3$)$_2$), –3.1 (Mg*C*H(SiMe$_3$)$_2$). Anal. Calc. for $C_{54}H_{86}MgN_2OSi_4$ (915.9): C, 70.81; H, 9.46; N, 3.06%. Found: C, 70.79; H, 9.36; N, 2.95%.

*Synthesis of **4***. 50 mg of [Ca{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (99.8 μmol) and 50 mg of **I** (99.8 μmol) were dissolved in C_6D_6. The reaction mixture turns instantly dark green. ^{1}H NMR data showed the clean formation of complex **4** as the sole product of the reaction (NMR yield > 99%). The reaction was scaled up ([Ca{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] 1.00 g, 2 mmol; **I** 1.00 g, 2 mmol), and stirred for 10 minutes at room temperature in toluene prior to removal of the solvent *in vacuo*. As the product refused to crystallize in 0.2 mL of pentane at –30 ^{o}C over a period of several weeks, complex **4** was used as a crude green solid, whose purity was confirmed by NMR spectroscopy and elemental analysis data. ^{1}H NMR ppm (C_6D_6): 7.15–7.26 (m, 6H, Ar-*H*), 6.46 (d, 1H, *H-3'*, ^3J = 7.7 Hz), 6.06 (t, 1H, *H-4'*, ^3J = 7.7 Hz), 5.43–5.47 (m, 2H, *H-5'* + *H-3*), 4.96 (dd, 1H, $^3J_{cis}$ = 10.2, ^3J = 4.4 Hz), 4.12 (m, 1H, *H-5*), 3.62 (sept, 2H, ^{i}Pr-C*H*Me$_2$, ^3J = 6.8 Hz), 3.51 (broad m, THF), 3.24 (sept, 2H, ^{i}Pr-C*H*Me$_2$, ^3J = 6.7 Hz), 1.49 (d, 6H each, ^{i}Pr-C*H*$_3$, ^3J = 6.7 Hz), 1.41 + 1.34 (two d, 3H each, ^{i}Pr-C*H*$_3$, ^3J = 6.8 Hz), 1.18-1.31 (m, 20H, THF + ^{i}Pr-C*H*$_3$), 0.48 (d, 1H, CC*H*(SiMe$_3$)$_2$, ^3J = 1.6 Hz), 0.21 (s, 18H, CaCH(Si*Me*$_3$)$_2$), 0.04 + 0.00 (two s, 9H each, CCH(Si*Me*$_3$)$_2$), –1.72 (s, 1H, CaC*H*(SiMe$_3$)$_2$). ^{13}C{^{1}H} NMR ppm (C_6D_6): 181.7 (*C-1'*), 150.1, 149.7, 148.2, 146.1, 143.3, 142.7, 138.8, 137.0, 132.5 (*C-3'*), 131.2, 126.4, 126.2, 124.5, 124.5 (*C-3*), 124.4, 124.0, 123.8, 123.5 (*C-4*), 123.1, 122.7 (*C-5'*), 122.6 (*C-4'*), 110.7 (*C-2*), 69.6 (THF, very broad), 38.3 (*C-5*), 29.3 + 29.2 + 28.9 + 28.5 (^{i}Pr-*C*HMe$_2$), 26.0 + 25.6 + 25.3 + 25.2 + 25.2 + 24.7 + 24.4 + 24.3 (^{i}Pr-*C*H$_3$), 25.3 (THF), 23.4 (C*C*H(SiMe$_3$)$_2$), 14.3 (Ca*C*H(SiMe$_3$)$_2$), 6.1 (CaCH(Si*Me*$_3$)$_2$), 2.1 + 1.0 (CCH(Si*Me*$_3$)$_2$). Anal. Calc. for $C_{58}H_{94}CaN_2O_2Si_4$ (1003.8): C, 69.40; H, 9.44; N, 2.79%. Found: C, 69.34; H, 9.34; N, 2.73%.

*Synthesis of **5***. 50 mg of [Sr{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (90.8 μmol) and 45 mg of **I** (90.8 μmol) were dissolved in C_6D_6. The reaction mixture instantly turns dark green. Analysis by ^{1}H NMR spectroscopy showed the clean formation of complex **5** as the sole product of the reaction (NMR yield > 99%). The reaction was scaled up ([Sr{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] 551 mg, 1 mmol; **I** 0.50 g, 1 mmol), and stirred for 10 minutes at room temperature in toluene prior to removal of the solvent *in vacuo*. As the product refused to crystallize in 0.2 mL of pentane at –30 ^{o}C over a period of several weeks, complex **5** was used as a crude green solid,

whose purity was confirmed by NMR spectroscopy and elemental analysis data. ^{1}H NMR ppm (C_6D_6): 6.97–7.16 (m, 6H, Ar-*H*), 6.45 (d, 1H, *H-3′*, ^{3}J = 7.7 Hz), 6.06 (t, 1H, *H-4′*, ^{3}J = 7.7 Hz), 5.41 (dd, 1H, *H-3*, $^{3}J_{cis}$ = 10.2 Hz, ^{4}J = 2.1 Hz), 5.40-5.42 (m, 1H, *H-5′*), 4.89 (dd, 1H, *H-4*, $^{3}J_{cis}$ = 10.2, ^{3}J =4.6 Hz), 4.15 (m, 1H, *H-2*), 3.68 (sept, 2H, ^{i}Pr-C*H*Me$_2$, ^{3}J = 6.8 Hz), 3.37 (broad m, THF), 3.27 (sept, 2H, ^{i}Pr-C*H*Me$_2$, ^{3}J = 6.7 Hz), 1.53 + 1.52 (two d, 3H each, ^{i}Pr-C*H*$_3$, ^{3}J = 6.7 Hz), 1.38 + 1.36 (two d, 3H each, ^{i}Pr-C*H*$_3$, ^{3}J = 6.8 Hz), 1.25–1.31 (m, 20H, ^{i}Pr-C*H*$_3$ + THF), 0.49 (d, 1H, CC*H*(SiMe$_3$)$_2$, ^{3}J = 1.6 Hz), 0.30 (s, 18H, SrCH(Si*Me*$_3$)$_2$), 0.06 + –0.01 (two s, 9H each, CCH(Si*Me*$_3$)$_2$), –1.86 (s, 1H, SrC*H*(SiMe$_3$)$_2$). ^{13}C{^{1}H} NMR ppm (C_6D_6): 181.1 (*C-1′*), 151.1, 150.2, 149.0, 146.9, 143.3, 142.6, 138.6, 138.4, 132.4 (*C-3′*), 131.0, 126.3, 125.9, 124.5 (*C-5′*), 124.2, 124.3, 123.7, 123.1, 123.0, 122.9 (*C-3*), 122.5 (*C-4*), 122.2 (*C-4′*), 109.5 (*C-2*), 69.4 (THF, very broad), 38.4 (*C-5*), 29.5 + 29.3 + 29.0 + 28.6 (^{i}Pr-*C*HMe$_2$), 26.0 + 25.7 + 25.4 + 25.3 + 25.2 + 24.9 + 24.4 + 24.3 (^{i}Pr-*C*H$_3$), 25.3 (THF), 23.6 (C*C*H(SiMe$_3$)$_2$), 19.1 (Sr*C*H(SiMe$_3$)$_2$), 6.4 (SrCH(Si*Me*$_3$)$_2$), 2.2 + 1.1 (CCH(Si*Me*$_3$)$_2$). Anal. Calc. for $C_{58}H_{94}N_2O_2Si_4Sr$ (1051.3): C, 66.26; H, 9.01; N, 2.66%. Found: C, 66.33; H, 8.97; N, 2.70%.

Synthesis of ***6***. 50 mg of [Ba{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (83.3 μmol) and 42 mg of **I** (83.3 μmol) were dissolved in C_6D_6. The reaction mixture turns instantly dark green. ^{1}H NMR data evidenced the presence of three components among which were the heteroleptic barium alkyl complex, **6** (ca. 70%), and the homoleptic barium complex, **7** (ca. 20%). Upon recrystallization of the crude mixture from toluene at –30 ^{o}C for a week, orange crystals of compound **8** suitable for X-ray diffraction analysis were isolated from the reaction mixture. The isolated amount of **8** was, however, insufficient for the acquisition of either NMR or elemental analysis data. Although attempts to separate **6** and **7** by fractional crystallization failed preventing the acquisition of elemental analysis data for compound **6**, compound **7** was synthesized and analyzed by independent methods (*vide infra*). ^{1}H NMR ppm (C_6D_6) for **6**: 7.08–7.23 (m, 6H, Ar-*H*), 6.48 (d, 1H, *H-3′*, ^{3}J = 7.7 Hz), 6.08 (t, 1H, *H-4′*, ^{3}J = 7.7 Hz), 5.47–5.51 (m, 2H, *H-5′* + *H-4*), 4.88 (dd, 1H, *H-4*, $^{3}J_{cis}$ = 10.2, ^{3}J = 4.4Hz), 4.21 (m, 1H, *H-5*), 3.69 (sept, 2H, ^{i}Pr-C*H*Me$_2$, ^{3}J = 6.8 Hz), 3.32 (broad m, 8H, THF), 3.27 (sept, 2H, ^{i}Pr-C*H*Me$_2$, ^{3}J = 6.7 Hz), 1.53 + 1.49 (two d, 3H each, ^{i}Pr-C*H*$_3$, ^{3}J = 6.7 Hz), 1.37 + 1.34 (two d, 3H each, ^{i}Pr-C*H*$_3$, ^{3}J = 6.8 Hz), 1.22-1.32 (m, 20H, THF + ^{i}Pr-C*H*$_3$), 0.50 (d, 1H, CC*H*(SiMe$_3$)$_2$, ^{3}J = 1.6 Hz), 0.29 (s, 18H, BaCH(Si*Me*$_3$)$_2$), 0.09 + 0.04 (two s, 9H each, CCH(Si*Me*$_3$)$_2$), –1.73 (broad s, 1H, BaC*H*(SiMe$_3$)$_2$). ^{13}C{^{1}H} NMR ppm (C_6D_6): 179.9 (*C-1′*), 150.8, 149.8, 148.8, 147.0, 143.2, 142.7, 138.0, 135.7, 132.2 (*C-3′*), 131.1, 126.1, 125.6,

124.4 (*C-5'*), 124.2, 124.0, 123.9, 123.8, 123.6, 123.2, 122.9 (*C-3*), 122.6 (*C-4*), 122.0 (*C-4'*), 107.5 (*C-2*), 68.3 (THF, very broad), 38.4 (*C-5*), 33.8 (Ba-CH(Si*Me*$_3$)$_2$), 29.6 + 29.5 + 29.0 + 28.8 (^{i}Pr-*C*HMe$_2$), 25.6 + 25.5 + 25.2 + 25.1 + 25.0 + 24.9 + 24.5 + 24.3 (^{i}Pr-*C*H$_3$), 25.4 (THF), 23.8 (C*C*H(SiMe$_3$)$_2$), 6.1 (Ba*C*H(SiMe$_3$)$_2$), 2.2 + 1.4 (CCH(Si*Me*$_3$)$_2$).

Independent synthesis of ***7****.* a) 15 mg of [Ba{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (25.0 μmol) and 25 mg of **I** (50 μmol) were dissolved in d$_8$-toluene at room temperature. After 10 minutes the solution had turned a homogeneous dark green. Analysis by ^{1}H NMR spectroscopy showed the clean formation of **7** as the sole product of the reaction. b) [KCH(SiMe$_3$)$_2$] (300 mg, 1.50 mmol) and [Ba{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (455 mg, 0.75 mmol) were stirred in THF at room temperature for 24 hours prior to removal of the solvent *in vacuo* and extraction into toluene. Removal of the solvent yielded complex **7** as a crude dark green solid whose ^{1}H NMR spectrum was reminiscent of that obtained from the reaction described in a). ^{1}H NMR ppm (d$_8$-tol): 6.84–7.32 (m, 12H, Ar-*H*), 6.46 (d, 2H, *H-3'*, ^3J = 7.7 Hz), 6.00 (t, 2H, *H-4'*, ^3J = 7.7 Hz), 5.34 (dd, 2H, *H-5'*, ^3J = 7.7 Hz, ^4J = 4.2 Hz), 5.17 (dd, 2H, *H-3*, $^3J_{cis}$ = 10.2 Hz, ^4J =1.5 Hz), 4.77 (dd, 2H, *H-4*, $^3J_{cis}$ = 10.2, ^3J = 4.3 Hz), 4.16 (broad s, 2H, *H-5*), 3.46–3.62 (m, 12H, THF + ^{i}Pr-C*H*Me$_2$), 3.09 (sept, 4H, ^{i}Pr-C*H*Me$_2$, ^3J = 6.6 Hz), 1.45 (m, 8H, THF), 1.38 + 1.35 (two d, 6H each, ^{i}Pr-C*H*$_3$, ^3J = 6.7 Hz), 1.24 (d, 6H, ^{i}Pr-C*H*$_3$, ^3J = 6.8 Hz), 1.03-1.14 (m, 30H, ^{i}Pr-C*H*$_3$), 0.49 (broad s, 2H, C*H*(SiMe$_3$)$_2$, ^3J = 1.6 Hz), 0.02 + -0.04 (two s, 9H each, Si*Me*$_3$). ^{13}C{^{1}H} NMR ppm (d$_8$-tol): 180.3 (*C-1'*), 151.0, 150.70, 150.69, 149.9, 147.69, 147.64, 143.7, 143.25, 143.22, 138.73, 138.70, 138.61, 138.56, 138.15, 138.23, 137.47, 137.57, 132.5, 131.1, 126.7, 126.0, 124.9, 124.65, 124.71, 124.6, 123.77, 123.73, 123.5, 122.3, 122.1, 109.22, 109.19, 68.0 (THF, broad), 38.8 (*C-5*), 29.9 + 29.7 + 29.5 + 29.1 +28.8 (^{i}Pr-*C*HMe$_2$), 26.24 + 26.18 + 26.11 + 25.9 + 25.5 + 24.4 + 23. 8 (^{i}Pr-*C*H$_3$), 25.1 (THF), 23.4 + 23.2 (*C*H(SiMe$_3$)$_2$), 2.8 + 1.3 (Si*Me*$_3$). Repeated attempts at obtaining elemental analysis for this complex failed due to its extreme air- and moisture-sensitivity.

Independent synthesis of ***9****.* Complex **1** (1.05 g, 1.50 mmol) and CaI$_2$ (220 mg, 0.75 mmol) were stirred in THF at room temperature for 24 hours prior to removal of the solvent *in vacuo* and extraction into hexane. Removal of the solvent yielded complex **9** as a crude dark green solid which was recrystallized from a 10:1 toluene/THF mixture at –30 ^{o}C over several days, yielding complex **9** as a dark green solid (265 mg, 25%) in a first fraction and green single crystals in a second one (227 mg, 21%). Due to apparent fluxional behaviour in solution ^{1}H NMR resonances were extremely broad and ^{13}C{^{1}H} NMR signals too weak for analysis. ^{1}H NMR (C$_6$D$_6$): 6.99–7.25 (m, 12H, Ar-*H*), 6.45 (broad d, 2H, *H-3'*, ^3J = 7.7 Hz), 6.05 (broad t,

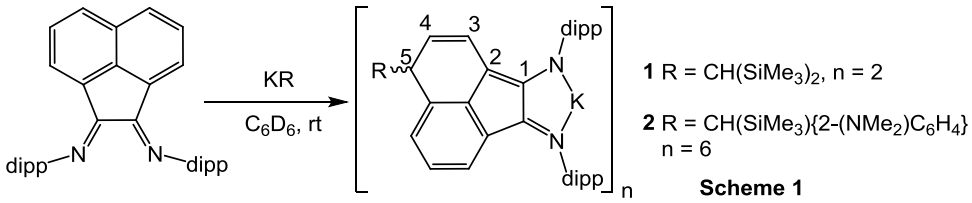
2H, *H-4'*, ^{3}J = 7.7 Hz), 5.23-5.38 (broad m, 4H, *H-3/4*), 4.99 (broad d, 2H, *H-5'*, ^{3}J = 7.7 Hz), 4.18 (s, 2H, *H-5*), 3.60 (broad m, 4H, THF), 2.99–3.44 (broad m, 8H, ^{i}Pr-C*H*Me$_2$), 0.68–1.34 (broad m, 52H each, ^{i}Pr-C*H*$_3$ + THF), 0.51 (broad s, 1H, CC*H*(SiMe$_3$)$_2$), 0.05 + –0.04 (two broad s, 9H each, CCH(Si*Me*$_3$)$_2$). Anal. Calc. for $C_{90}H_{126}CaN_4OSi_4$ (1432.4): %C, 75.46; H, 8.87; N, 3.91%. Found: C, 75.29; H, 8.74; N, 3.84%.

Notes on X-ray crystallographic refinements

Single crystal X-ray diffraction data were collected at 150 K on a Nonius KappaCCD diffractometer, equipped with an Oxford Cryosystem, using graphite-monochromated Mo Kα radiation (λ =0.71073 Å). Data were processed using the Nonius Software.[29] Crystal data, data collection and refinement parameters for 2, 8, and 9 are presented in Table **1**. Structure solution, followed by full-matrix least-squares refinement, was performed using the WINGX-1.80 suite of programs throughout.[30] Compound **1**: The dimer co-crystallized with one solvent molecule of toluene. Compound **2**: The asymmetric unit contains 1/6 of a hexameric complex. It also contains one toluene solvent molecule with 50% occupation, disordered over a two-fold axis. Another toluene molecule is disordered about a three-fold axis with 33% occupation. Traces of a further a solvent molecule were located over a three-fold axis but could not be properly solved. The very large crystal diffracted very well at low angle but presented a falloff in intensity above $2\theta = 35^{o}$. As a consequence the solvent disorders could not be solved satisfactorily. The PLATON program SQUEEZE was employed to account for the solvent-containing voids. Checkcif detected a potential disorder in one of the isopropyl groups (C39–C41). Due to the lack of high angle intensity data this could not be properly solved. Compound **9**. The crystal was small and only weakly diffracting, hence the high R(int). The asymmetric unit contained the main complex and three solvent molecules; two half-occupied THF molecules (bond lengths to O3 had to be restrained) and one benzene molecule disordered over two sites in a 63:37 ratio. Atoms of the minor part of the disordered benzene were refined isotropically. ADP for C122 had been restrained.. All methyl groups of the bis(trimethylsilyl)methyl substituent containing Si1 and Si2 displayed rotational disorder in a 42:58 ratio. Si-C bond lengths herein have been restrained as well as ADPs of C39 and C43.

Results and discussion

Addition of the potassium alkyl precursors [KCH(SiMe$_3$)$_2$] and [KCH(SiMe$_3$){2-(NMe$_2$)C$_6$H$_4$}] to an orange suspension of **I** in C$_6$D$_6$ resulted in a rapid color change to form a clear, dark green solution (Scheme 2). In both cases analysis by ^{1}H NMR spectroscopy showed quantitative conversion of the starting materials to a single potassium complex, compounds **1** and **2**, respectively, displaying six distinct multiplets in the region from 4.4 to 6.5 ppm, characteristic of selective dearomatization of the acenaphthene backbone and alkyl functionality transfer. The alkylation site of the ligand backbone was identified by a COSY experiment as the C^5 position (Scheme 2), which was confirmed by two subsequent X-ray diffraction experiments (*vide infra*). Alkylation at this position generated a chiral center which caused the two magnetically inequivalent (Si(C*H*$_3$)$_3$) groups in both complexes to appear as two separate (9H) singlets. The asymmetric nature of the new imine-amido ligand system also caused splitting of the *iso*-propyl methine and methyl resonances, both in the ^{1}H and ^{13}C{^{1}H} NMR spectra. In the case of complex **2** the presence of a second chiral center at the methine position of the 1-trimethylsilyl-*o*-dimethylaminobenzyl substituent led to the formation of a ca. 9:1 mixture of two diastereomers as determined by integration of the ^{1}H NMR spectrum.



Scheme 1

Re-crystallization at room temperature in toluene afforded large dark green crystals of compounds **1** and **2** suitable for X-ray diffraction. Although the structure of compound **1** was described in our earlier communication,[24] and will, thus, not be described in detail here, selected bond length and angle data for both compounds are listed in Table 2 for purposes of comparison. While Compound **1** comprised a centrosymmetric dimer in the solid state, compound **2** assembles as a hexameric array in which coordination between molecules is provided by a η^3-interaction between a N$_2$-coordinated potassium atom and the C30, C34 and C35 carbon atoms of the alkylated backbone ring of the adjacent complex, with a K–centroid distance of 2.884(5) Å (Figure1). Compound **2** crystallizes as a single (*R*,*S*)/(*S*,*R*) diastereomeric couple which, based on the crystalline yield (~80%) and its ^{1}H NMR spectrum, was identified as the major diastereomer. In contrast to potassium complex **1** the

K–N bond lengths in compound **2** reflect the asymmetric binding of the alkylated imine-amido ligand [K–N_{imine} 2.762(4); K–N_{amide} 2.702(4) Å].

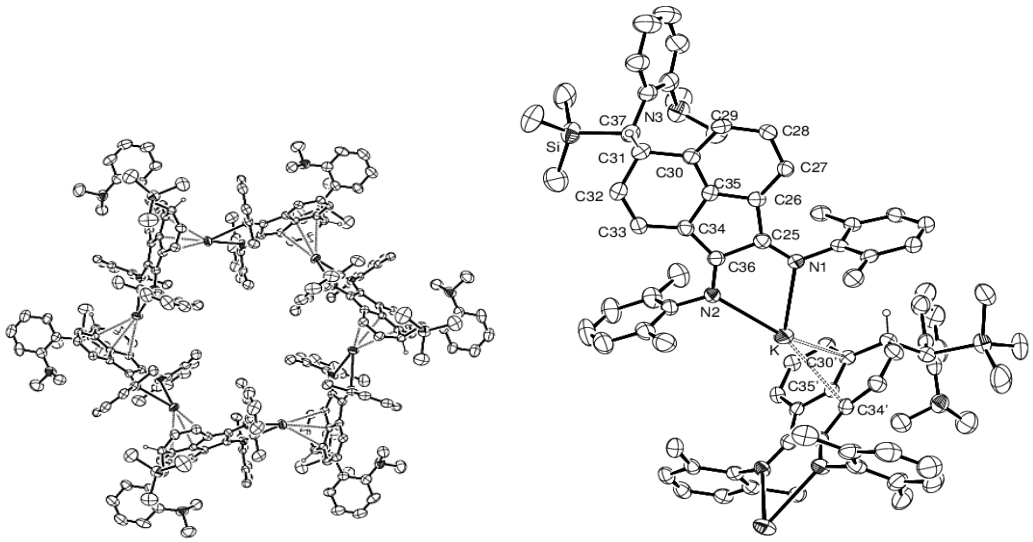


Figure 1. ORTEP representation of compound **2**: hexameric array (left), two-molecule binding motif (right). Thermal ellipsoids drawn at 30% probability. *Iso*-propyl methyl groups and hydrogen atoms omitted except for those attached to chiral centers C31 and C37.

Table 1 Crystal Data, Data Collection and Refinement Parameters for **2**, **8**, and **9**

Compound reference	**2**	**8**	**9**
Chemical formula	$C_{288}H_{360}K_6N_{18}Si_6$	$C_{86}H_{118}N_4Si_4$	$C_{90}H_{126}CaN_4OSi_4$•C_4H_8O•C_6H_6
Formula Mass	4477.08	1320.20	1582.60
Crystal system	Cubic	Trigonal	Triclinic
a/Å	39.6750(7)	13.7376(4)	17.3947(6)
b/Å	39.6750(7)	13.7376(4)	18.2532(9)
c/Å	39.6750(7)	37.1695(13)	19.0363(9)
α/°	90.00	90.00	116.153(2)
β/°	90.00	90.00	108.911(2)
γ/°	90.00	120.00	91.946(2)
Unit cell volume/Å^3	62452.6(19)	6074.9(3)	5020.1(4)
Temperature/K	150(2)	150(2)	150(2)
Space group	*I a* $\bar{3}$	*P* 3_1 2 1	*P* $\bar{1}$
No. of formula units per unit cell, *Z*	8	3	2
Absorption coefficient, *μ*/mm^{-1}	0.154	0.118	0.156
No. of reflections measured	55758	28082	79347
No. of independent reflections	9182	7053	17520
R_{int}	0.1026	0.0931	0.1864
Final R_1 values ($I > 2\sigma(I)$)	0.1001	0.0684	0.0955
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2422	0.1120	0.2243
Final R_1 values (all data)	0.1786	0.1416	0.2062
Final $wR(F^2)$ values (all data)	0.2848	0.1325	0.2908
Goodness of fit on F^2 [e]	1.037	1.015	1.026
Flack parameter	-0.03(15)		

[a] $F_C^* = k F_C[1 + 0.001F_C^2\lambda^3/\sin(2\theta)]^{-1/4}$. [b] Flack, H.D. Acta Crystallogr. A **1983**, 39,876.

[c] $R_1 = \Sigma ||F_O|-|F_C||/\Sigma|F_O|$. [d] $wR_2 = \{\Sigma[w(F_O^2 - F_C^2)^2] / \Sigma[w(F_O^2)^2]\}^{1/2}$.

[e] GOF = $S = \{\Sigma[w(F_O^2 - F_C^2)^2]] / (n-p)\}^{1/2}$.

Table 2 Selected Bond Lengths (Å) and Angles (°) for Compounds **1, 2**, **8** and **9**

	1[a]	**2**[a]	**8**	**9**[b]
M–N1	2.694(3)	2.702(4)	–	2.571(4)
M–N2	2.703(3)	2.762(4)	–	2.372(4)
N1–C25	1.281(4)	1.267(5)	1.263(4)	1.286(7)
N2–C36	1.335(4)	1.318(5)	1.283(5)	1.355(7)
C34–C36	1.393(4)	1.415(6)	1.487(5)	1.418(8)
C30–C31	1.533(5)	1.524(6)	1.523(5)	1.519(8)
C31–C32	1.517(5)	1.514(7)	1.563(5)	1.510(9)
C32–C33	1.351(5)	1.390(6)	1.501(5)	1.345(8)
M–centroid	2.866(4)	2.884(5)	–	–
C32–C32'	–	–	1.557(6)	–
N1–M–N2	63.52(8)	61.95(11)	–	70.07(15)
M–N1–C25	118.2(2)	119.7(3)	–	109.6(3)
M–N2–C36	117.4(2)	118.2(3)	–	114.7(3)
N1–C25–C36	121.7(3)	119.0(4)	122.0(3)	121.6 (5)
C30–C31–C32	111.6(3)	109.6(4)	114.4(3)	111.7(5)
C30–C31–C37	113.4(3)	110.5(4)	114.7(3)	113.7(5)
C32–C31–C37	111.3(3)	109.7(4)	110.1(3)	111.8(5)
C31–C32–C33	–	–	117.9(3)	126..3(6)
C33–C32–C32'	–	–	109.9(2)	–
C31–C32–C32'	–	–	110.7(4)	–

[a] M = K [b] M = Ca

In a similar manner to the potassium-based reactions, addition of $[M\{CH(SiMe_3)_2\}_2(THF)_2]$ (M = Ca, Sr) to a suspension of **I** in C_6D_6 resulted in instant solubilization of the starting materials and a rapid color change to dark green. The analogous reaction with $[Mg\{CH(SiMe_3)_2\}_2(THF)_2]$ required 24 hours heating at 60 °C to yield the same result (Scheme 2). In all three cases ^{1}H NMR spectra were reminiscent of that of **1**, showing clean formation of the heteroleptic alkaline earth organometallic species **3**, **4** and **5**, with the additional (18H) and (1H) singlets of the metal-bound monoanionic $[CH(SiMe_3)_2]^-$ co-ligand at ca. 0.3 ppm and –1.7 ppm respectively (Figure 2).

Scheme 2

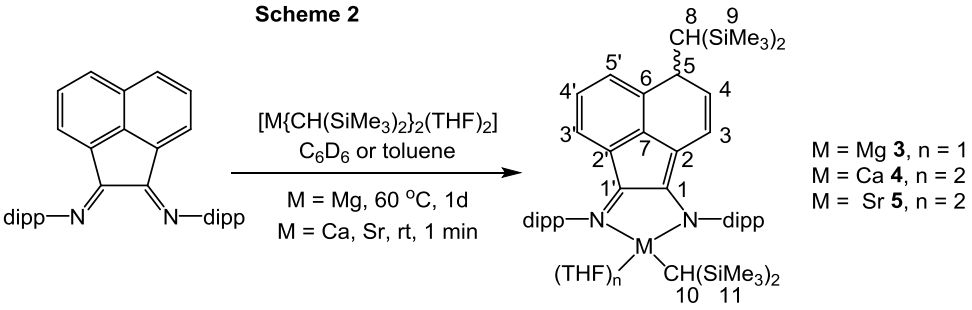
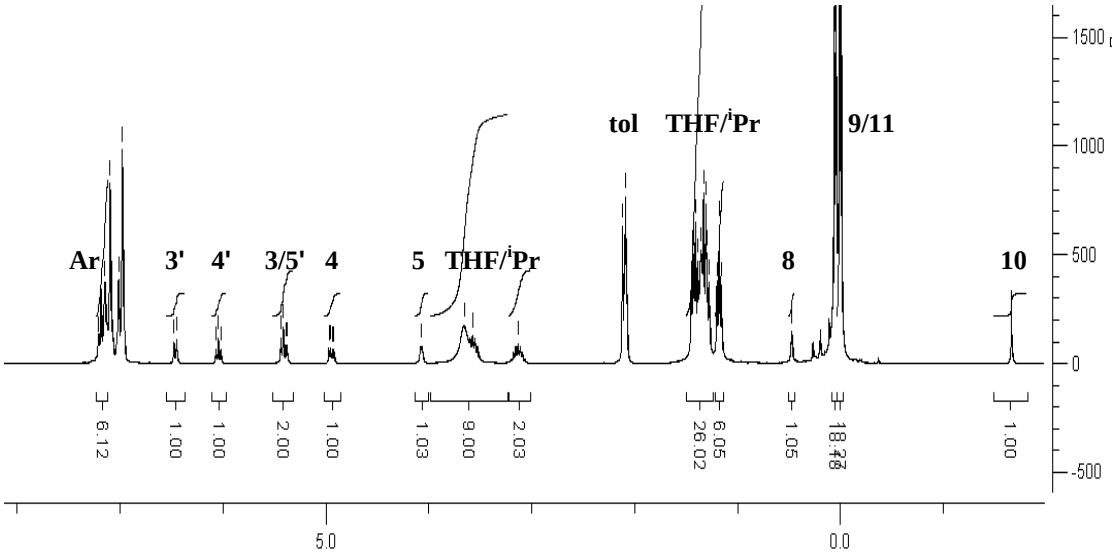
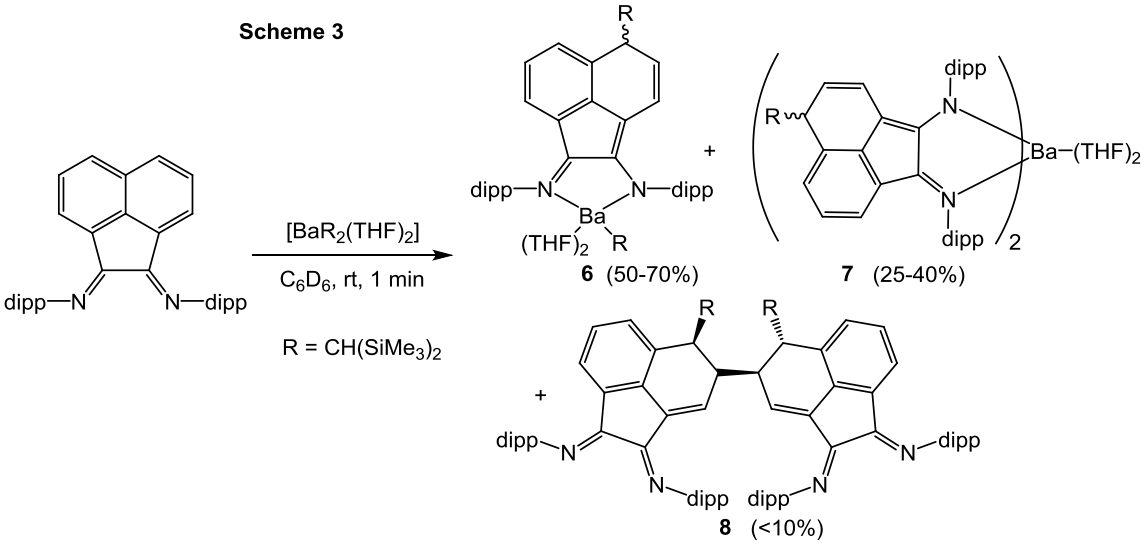


Figure 2. Annotated ^{1}H NMR spectrum of the dearomatized calcium complex **4**.



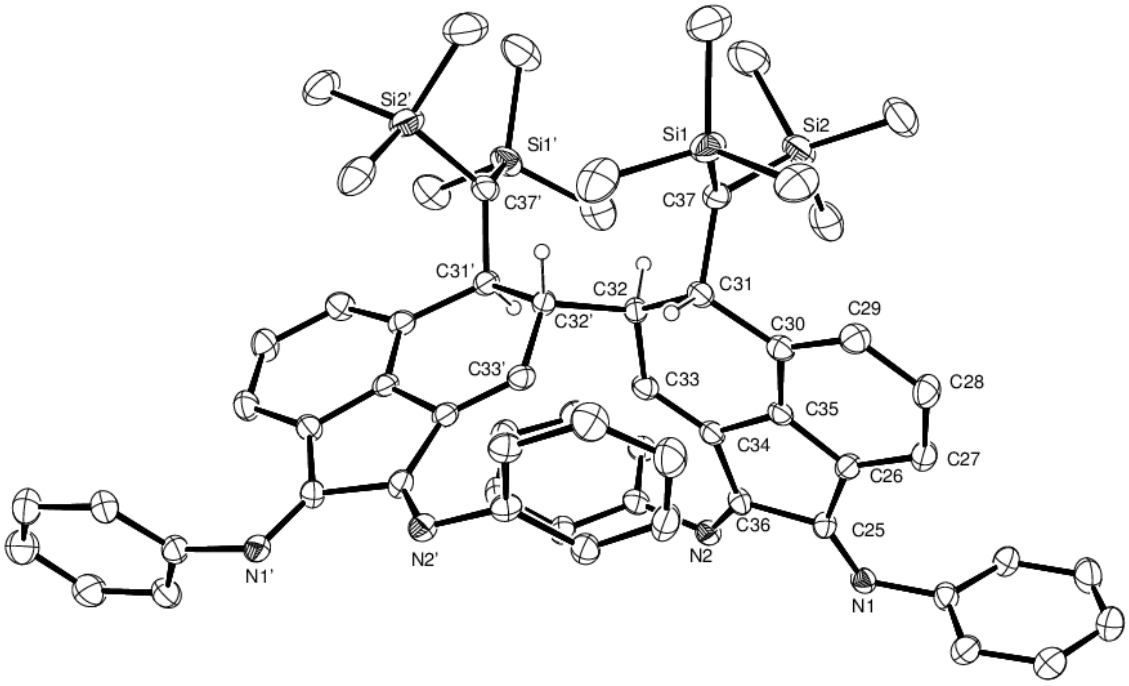
Although an analogous reaction with the barium dialkyl precursor, [Ba{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$], also led to an instant color change to dark green, ^{1}H NMR data at the first point of analysis showed the formation of three distinct dearomatized species, among which the heteroleptic barium alkyl complex **6** (50–70% conversion) was identified by the characteristic upfield BaC*H*(SiMe$_3$)$_2$ proton shift at –1.73 ppm (Scheme 3). A subsequent independent synthesis of the homoleptic barium complex, **7**, from the reaction between two equivalents of **I** and [Ba{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] enabled the identification of the second component of the reaction mixture as complex **7**, present in 25–40% yield.

Scheme 3



A third product, present in up to 10% yield, was only identified after storage of the reaction mixture in a 1:2 toluene/hexane solution at –30 ^{o}C over several days provided orange crystals suitable for X-ray diffraction analysis. The result of this experiment, displayed in Figure, shows two C^5-alkylated dearomatized BIAN ligands coupled at the C^4 position. Selected bond length and angle data are provided inTable 2. Compound **8** crystallizes as a single (4*R*, 4'*R*, 5*S*, 5'*S*) enantiomer (absolute structure parameter = 0.03(15)) in the chiral space group *P* 3_1 2 1. As in the ligand precursor, both N–C bond lengths [1.263(4), 1.283(5) Å] are indicative of imine bonds. The presence of the two *pseudo*-tetrahedral sp^3 carbon centers, C31 [C30–C31–C32 114.4(3)^{o}; C30–C31–C37 114.7(3)^{o}; C32–C31–C37 110.1(3)^{o}] and C32 [C31–C32–C33 117.9(3)^{o}; C33–C32–C32' 109.9(2)^{o}; C31–C32–C32' 110.7(4)^{o}], induces a significant distortion of the alkylated C_6H_3 rings of the ligand backbones, accompanied by an increase in the C–C bond lengths [C30–C31 1.523(5); C31–C32 1.563(5); C31–C32 1.501(5) Å]. While we have not fully rationalized the synthesis of this chiral, dimerized tetra-imine product, we suggest its formation is possibly the result of a sterically induced radical coupling reminiscent of well precedented reactivity observed for similarly redox inactive 4f-element complexes.[31] In support of this hypothesis, Evans and Cowley have observed a radical anion C^5-alkylated free radical as an intermediate in the formation of the dialkylated dearomatized lithium complex, **V**.[16]

Figure 3. ORTEP representation of compound **8**. Thermal ellipsoids drawn at 30% probability. *Iso*-propyl groups and hydrogen atoms omitted except for those attached to the chiral centers C31 and C32.



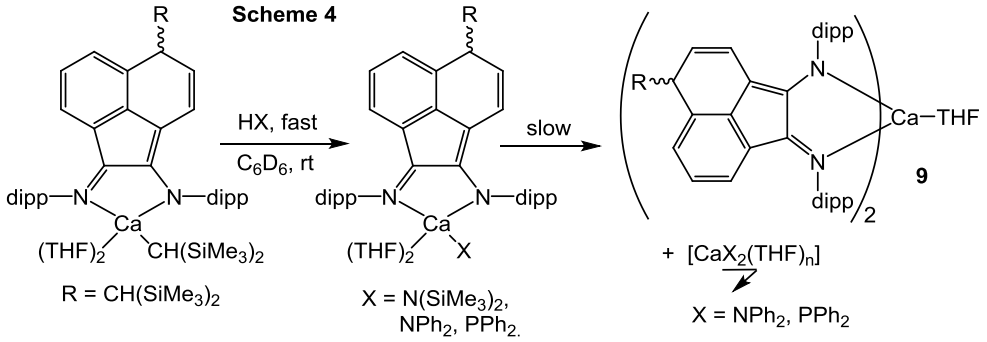
Multiple attempts to obtain crystals of the alkaline earth organometallic complexes **3 – 6** suitable for X-ray analyses were thwarted by the extreme solubility of these compounds even after months of storage at –30 ^{o}C in minimal amounts of hydrocarbon solvents such as hexane or pentane. NMR data and elemental analyses of the crude magnesium, calcium and strontium products, however, left no doubt as to their formulation. Attempts to recover the alkylated amino-imine ligand by controlled hydrolysis of the organometallic complexes initially led to a color change from green to purple, followed by a gradual change towards dark red over a period of several hours. ^{1}H NMR data and later recrystallization of the crude product from toluene evidenced quantitative conversion to the rearomatized ligand precursor, **I**, with formation of the alkane $CH_2(SiMe_3)_2$. Although the mechanism of this reaction remains to be elucidated it is possible that the high stability of the aromatic BIAN ligand may be the driving force of this de-alkylation process.

The kinetic stability of the heteroleptic complexes **3**, **4** and **5** was assessed by heating a d_8-toluene solution of these compounds at 80 ^{o}C for a week. Apart from a slight amount of protonolysis of the alkyl ligand to form the alkane $CH_2(SiMe_3)_2$ in the cases of **4** and **5** (< 5%), possibly due to reaction with the solvent, the ^{1}H NMR spectra remained virtually unchanged, suggesting an absence of Schlenk-type ligand redistribution processes. Addition

of two equivalents of the ligand precursor to one equivalent of the magnesium, calcium or strontium dialkyl species in d_8-toluene did not yield the expected homoleptic complexes at room temperature. Rather, the heteroleptic complexes **3**, **4** and **5** were formed while the excess ligand remained unreacted. Heating of these mixtures at 90 ^{o}C over a period of several days also did not result in reaction with the second equivalent of ligand.

Stoichiometric NMR scale reactions of calcium complex **4** with protic substrates such as hexamethyldisilazane, diphenylamine or diphenylphosphine in C_6D_6 resulted in immediate protonolysis of the alkyl co-ligand, as observed in the ^{1}H NMR spectra by the disappearance of the upfield Ca*CH*$(SiMe_3)_2$ singlet at –1.72 ppm and the appearance of the characteristic alkane resonance at –0.2 ppm (Scheme 4). Given the comparable steric demands of the bis(trimethylsilyl)amide and bis(trimethylsilyl)methanide co-ligands, the resulting heteroleptic calcium bis(trimethylsilyl)amide complex evidenced solution stability similar to complex **4**. In contrast, monitoring by ^{1}H NMR spectroscopy of the heteroleptic calcium complexes bearing the less sterically demanding diphenylamide and diphenylphosphide co-ligands under the same conditions suggested slow Schlenk-type ligand redistribution towards the homoleptic calcium species **9** characterized by the broadening and shifting of the dearomatized ligand backbone and *iso*-propyl resonances, accompanied by precipitation of insoluble colorless products tentatively attributed to homoleptic calcium amide and phosphide species (Scheme 4) which are known to be insoluble in non-coordinating hydrocarbon solvents.[32] An independent synthesis of complex **9** by the reaction between two equivalents of potassium complex **1** and calcium iodide in THF confirmed the formation of **9** in both these reactions.

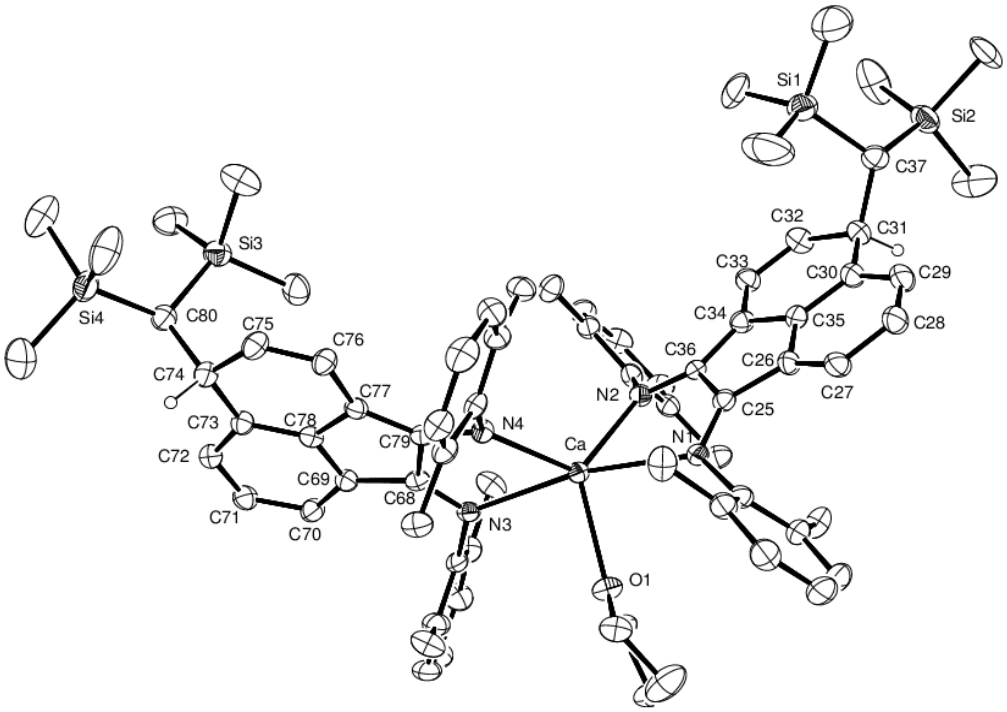
Scheme 4



Crystals of compound **9** suitable for X-ray diffraction analysis were obtained after storage in a 4:1 toluene/THF mixture at –30 ^{o}C for several weeks. The result of this experiment is displayed in Figure 4. Selected bond length and angle data are listed in Table 2. Compound **9** crystallizes as a mono-THF adduct and the five-coordinate calcium center

displays a highly distorted trigonal bipyramidal geometry with both imine nitrogen atoms in axial positions. The mean planes formed by the two almost planar ligand backbones form an angle of 82.8°. While in the case of complex **1** the KN_2C_2 ring remains planar, the presence of the large calcium center in **9** causes a slight distortion in the CaN_2C_2 rings. The N1–Ca–N2 and N3–Ca–N4 bite angles of the two alkylated BIAN ligands [70.07(15) and 69.65(14)°, respectively] are notably smaller than the N–Ca–N angles observed in calcium complexes supported by a doubly reduced BIAN ligand [75.76(7)–78.5(2)°][7f] or the homoleptic complex of the radical-anion [{**I**$^{\bullet}$}$_2$Ca] [73.58(9)°].[7g] The Ca–N_{imine} distances of 2.571(4) and 2.572(5) Å are substantially longer than the Ca–N_{amide} bonds of 2.372(4) and 2.354(5) Å, reflecting the stronger bonding between the metal center and the anionic amide moiety of the ligand. As in the potassium complex **1** the N2–C36 and N4–C79 bond lengths of the amide residues [1.355(7) and 1.347(7) Å] are significantly longer than the N1=C25 and N3=C68 bond lengths of the imine moieties [1.286(7) and 1.278(7)Å], while the ethanediylidyne bridges are slightly shorter in **9** than in **1** [**9** 1.489(8) and 1.509(8) Å; **1** 1.518(4) Å]. As previously observed for compound **1**, the dearomatization of the alkylated C_6H_3 rings only induces a slight distortion from planarity despite the presence of the sp^3 C31 and C74 carbon centers indicated by the elongated C–C bond lengths [C30–C31 1.519(8); C31–C32 1.510(9); C73–C74 1.522(8); C74–C75 1.497(8) Å] and the *pseudo*-tetrahedral angles [C32–C31–C30 111.7(5); C32–C31–C37 111.9(5); C30–C31–C37 113.7(5); C75–C74–C73 111.5(5); C75–C74–C80 112.0(5); C73–C74–C80 114.7(5)°].

Figure 4. ORTEP representation of compound **9**. Thermal ellipsoids drawn at 30% probability. *Iso*-propyl methyl groups and hydrogen atoms omitted except for those attached to the chiral centers C31 and C74.



Catalytic intramolecular hydroamination of hindered aminoalkenes

A preliminary comparison of turnover frequencies for the intramolecular hydroamination of 1-amino-2,2-diphenyl-4-pentene showed the calcium complex **4** to be by far superior to its magnesium and strontium analogues, with the order of reactivity being **4** > **5** >> **3** (Table 3, entries 1a–c). The same trend has been observed for the majority of previously described alkaline earth catalyzed hydroamination/cyclization reactions.[21,24,25,33] Complex **4** was then assessed for the intramolecular hydroamination of a wide range of substituted aminoalkenes on a NMR scale in C_6D_6 or d_8-toluene. In all cases careful inspection of the ^{1}H NMR spectra showed no change suggestive of ligand redistribution in the characteristic shifts of the dearomatized ligand backbone throughout the reaction times up to 80 ^{o}C, above which signs of Schlenk equilibria started to become apparent. As already observed in the case of homoleptic alkaline earth dialkyl precatalysts and the heteroleptic iminoanilide species **VIIa**–**c**, the reactive bis(trimethylsilyl)methanide co-ligand of **4** greatly increases reactions rates compared to homoleptic or heteroleptic calcium bis(trimethylsilyl)amide precatalysts.[21,24] This is due to the large p*K*a difference between $CH_2(SiMe_3)_2$ and the aminoalkene substrates leading to rapid and irreversible catalyst activation, as shown by the complete disappearance

of the distinctive up-field alkyl singlet at ca. –1.7 ppm within the first point of analysis in all these reactions. In contrast $HN(SiMe_3)_2$ may compete with the substrate for neutral coordination to the calcium center and reversible σ-bond metathesis.[33c,34] Furthermore the presence of the stabilizing dearomatized BIAN ligand leads to increased reactivity compared to the simple homoleptic precursor, $[Ca\{CH(SiMe_3)_2\}_2(THF)_2]$.[24] This positive spectator ligand effect has already been noted when comparing heteroleptic and homoleptic group 2 amide precatalysts,[24,33c] and is most pronounced with the iminoanilide species, **VIIa**–**c**, which remain the most reactive precatalysts reported for hydroamination/cyclization reactions.[21] Complex **4** displayed the usual reactivity trends depending on the substitution pattern of the aminoalkene substrate. Substrates providing a favorable Thorpe-Ingold effect – i.e. with larger digeminal *β*-substituents – required lower precatalyst concentrations and shorter reaction times (Table 3, entries 1–4). It is notable that the 2,2-diphenyl-substituted substrate provided essentially quantitative conversion to the corresponding pyrrolidine within the first point of analysis at room temperature using only 0.5 mol % of **4** (entry 1), while the simplest substrate, 1-amino-4-pentene, did not provide any reaction under the conditions tested (entry 4). In line with previous findings, catalytic turnover was also more efficient for smaller ring sizes, in the order of 5 > 6 >> 7 (entries 1b, 12b and 14b) and the calcium precatalyst, **4**, was prone to induce alkene isomerization to internal positions for longer aminoalkene chains (entries 13b, 14b). In contrast to this latter observation the magnesium analogue afforded complete selectivity for the cyclized product (entries 12a, 14a). As has been previously observed with heteroleptic alkaline earth *β*-diketiminato species the calcium pre-catalyst, **4**, proved incapable of effecting the cyclization of 1-amino-2,2-diphenyl-6-heptene to the corresponding hexahydroazepine, even under forcing conditions (entry 15b).[25,33a] In contrast the magnesium precatalyst, **3** (20 mol %), provided clean and near-quantitative conversion to the desired seven-membered *N*-heterocycle over 24 hours at 80 ^{o}C (entry 15a). In comparison the *n*-butyl magnesium *β*-diketiminate derivative required 5.5 days at 80 ^{o}C to achieve only 88% conversion.[25] Internal substitution of the alkene moiety only caused a small decrease in reactivity (entry 6), whereas the activated terminally substituted substrate, 1-amino-2,2,5-triphenyl-4-pentene, was smoothly converted to the corresponding pyrrolidine under even milder conditions than the parent 1-amino-2,2-diphenyl-4-pentene (entry 1b). Most notable, however, was the relative ease with which complex **4** catalyzed the intramolecular hydroamination of terminally substituted, unactivated substrates. While to date only $[Ca\{CH(SiMe_3)_2\}_2(THF)_2]$ has proved successful for he cyclization of 1-amino-2,2-diphenyl-4-hexene with modest yields under forcing conditions,[33c] complex **4** provided near-

quantitative conversion to the corresponding pyrrolidine within 5 hours at room temperature and only 5 mol % catalyst loading (entry 7). A marked Thorpe-Ingold effect was also apparent for these terminally substituted unactivated substrates. Although 4-methyl-2,2-diphenylpent-4-en-1-amine and (*E*)-2,2-diphenylhex-4-en-1-amine underwent smooth cyclization (entries 6 and 7), complete loss of catalytic activity was encountered in the case of 1-amino-2,2-dimethyl-4-hexene under the reaction conditions assessed (entry 9). The slightly more challenging terminal ethyl derivative, 1-amino-2,2-diphenyl-4-heptene, also underwent clean cyclization to 2-methyl-4,4-diphenylpyrrolidine, albeit at higher catalyst loading (10 mol %) and temperature (60 ^{o}C) (entry 10). The isomeric 1-amino-2,2-diphenyl-5-heptene, however, showed no sign of cyclization to the desired piperidine even at high catalyst loadings of **4** and elevated reaction temperatures (entry 13). Finally the precatalyst also proved efficient at the hydroamination of aminoalkenes bearing secondary amine functionalities, with little loss of activity, as shown by the facile cyclization of *N*-benzyl-1-amino-2,2-diphenyl-4-pentene (entry 15). In the cases of substrates which did not undergo cyclization (entries 4, 9, 11, 13, 14b) stoichiometric reactions between **4** and two or three equivalents of the aminoalkene led to instant protonolysis of the reactive alkyl ligand and ^{1}H NMR suggested the formation of stable heteroleptic amidoalkene complexes supported by the dearomatized BIAN ligand and one or two neutrally adducted aminoalkene ligands.

Conclusion

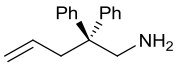
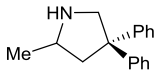
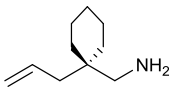
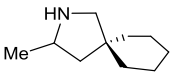
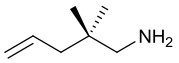
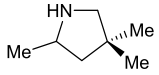
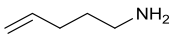
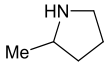
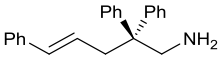
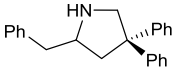
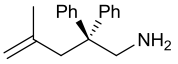
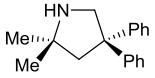
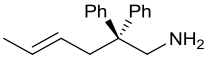
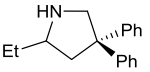
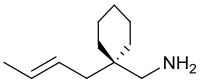
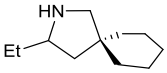
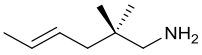
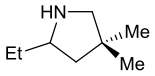
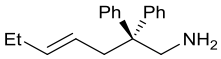
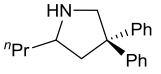
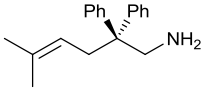
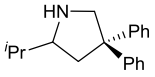
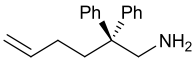
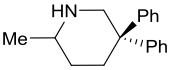
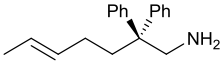
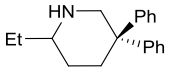
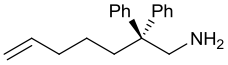
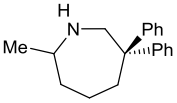
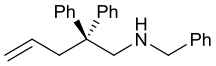
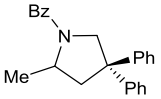
In conclusion we have shown that reactions of a dipp-substituted bis(imino)acenaphthene with a range of sterically demanding potassium alkyl or heavier alkaline earth dialkyl reagents result in facile dearomatization through alkyl transfer to the C^{5}-position of the conjugated acenaphthene system. The resultant heteroleptic group 2 derivatives display enhanced kinetic stability to Schlenk-type redistribution equilibria which we suggest is a consequence of both the steric demands of the *N*-dipp and the rigidity provided by the deraromatized fused ring acenaphthene ligand backbone. Facile solution exchange is encountered, however, when the.bis(trimethylsilyl)methyl substituent is replaced by an anionic ligand of lower overall steric demands. An assessment of the heteroleptic group 2 compounds as precatalysts for the intramolecular hydroamination of aminoalkenes evidences enhanced reactivity which we ascribe to the greater solution stability of the catalytically active species. Most notably the calcium species, **4**, may even be applied to the high yielding cyclization of substrates bearing alkyl substitution at either of the alkenyl positions. We are continuing to study this chemistry and to elaborate the application of these easily accessed

organometallic species to a broader spectrum of demanding stoichiometric and catalytic reactions.

Acknowledgement: We thank the Engineering and Physical Sciences Research Council for funding of this work (EP/I014519/1).

Supporting Information Available: Full experimental and instrument details. Characterization data for products of all catalytic cyclization reactions. Details of the X-ray diffraction analyses of compounds **1**, **2**, **8** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 3. Scope of intramolecular hydroamination with precatalysts **3**–**5**.

Entry	Substrate	Product	Catalyst (mol %)	Time (h)	T (^{o}C)	NMR yield (%)[a]
1a			**3** (0.5)	18	60	<5
1b			**4** (0.5)	0.25	25	>99
1c			**5** (0.5)	1	25	76
2			**4** (1.0)	0.3	25	99
3			**4** (2.0)	1	25	95
4			**4** (10.0)	24	80	0
5			**4** (0.25)	0.1	25	98
6			**4** (2.0)	1	25	98
7			**4** (5.0)	5	25	95
8			**4** (10.0)	18	60	93
9			**4** (10.0)	48	80	0
10			**4** (12.0)	40	60	98
11			**4** (20.0)	80	80	0
12a			**3** (5.0)	18	60	>99
12b			**4** (2.0)	1	25	85[b]
13			**4** (20.0)	48	80	0
14a			**3** (20.0)	24	80	95
14b			**4** (20.0)	48	80	0[c]
15			**4** (1.0)	0.5	25	98

[a] NMR yields were measured against an internal TMSS standard in C_6D_6 or d_8-toluene; [b] 11% isomerization to the internal aminoalkene; [c] 21% isomerization to the internal aminoalkene.

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